

Spreadsheet Based Scaling Calculations and Membrane Performance

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Abstract

Many membrane element manufacturers provide a computer program to aid buyers in the use of their elements. However, to date there are few examples of fully integrated public domain software available for calculating reverse osmosis and nanofiltration system performance. The Total Flux and Scaling Program (TFSP), written for Excel 97 and above, provides designers and operators new tools to predict membrane system performance, including scaling and fouling parameters, for a wide variety of membrane system configurations and feedwaters.

The TFSP development was funded under EPA contract 9C-R193-NTSX. It is freely downloadable at www.reverseosmosis.com/download/TFSP.zip. TFSP includes detailed calculations of reverse osmosis and nanofiltration system performance. Of special significance, the program provides scaling calculations for mineral species not normally addressed in commercial programs, including aluminum, iron, and phosphate species. In addition, ASTM calculations for common species such as calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), BaSO_4 , SrSO_4 , SiO_2 , and LSI are also provided.

Scaling calculations in commercial membrane design programs are normally limited to the common minerals and typically follow basic ASTM methods, which are for the most part graphical approaches adapted to curves. In TFSP, the scaling calculations for the less common minerals use subsets of the USGS PHREEQE and WATEQ4F databases and use the same general calculational approach as PHREEQE and WATEQ4F. The activities of ion complexes are calculated iteratively. Complexes that are unlikely to form in significant concentration were eliminated to simplify the calculations. The calculation provides the distribution of ions and ion complexes that is used to calculate an effective ion product "Q." The effective ion product is then compared to temperature adjusted solubility products (K_{sp} 's) of solids in order to calculate a Saturation Index (SI) for each solid of interest. The SI is expressed as a log value ($\log(Q) - \log(K_{sp})$) where positive values indicate potential scaling conditions. As this is an unprotected spreadsheet, the methodology is plainly visible to and readily modified by the user.

Calculation Methodology

General Comments

Although most of the major membrane manufacturers provide calculation programs designed for their specific membranes, the experienced engineer can often be well served by having the calculation methodology available for easy viewing and/or modification. A spreadsheet-based program therefore provides a useful tool to the water system engineer. The feedwater to a membrane system is rarely scaling before it is concentrated by a pass through membrane system. However, scaling becomes more likely as fluid concentrations increase and it is useful to be able to predict the concentrations of the various ions at all points in the system, particularly in the concentrate. In addition, it is important to estimate the effective concentration at the membrane surface, which is always higher than the bulk fluid concentration due to “concentration polarization.”

In this spreadsheet we use a combination of iterative and direct calculation methods to first estimate the performance of a given membrane system, then predict the concentrations of the solution at various points in the system, and finally compute a scale index for the species of interest.

Program Flow

The Program Flow is designed as follows:

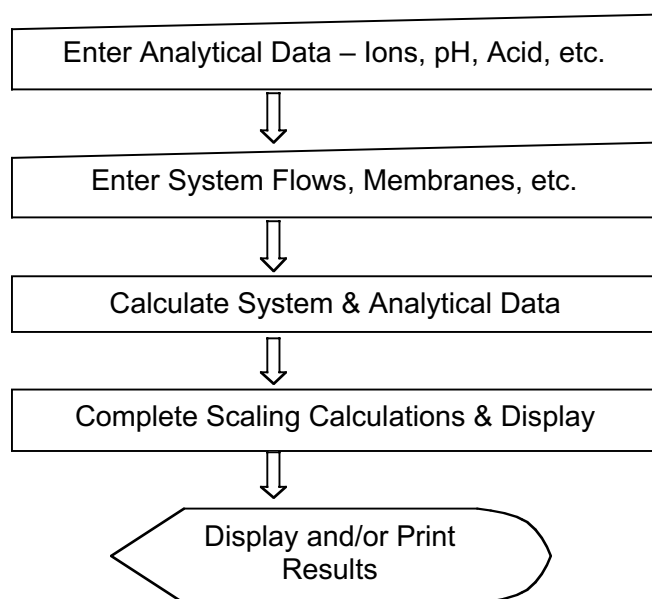


Figure 1 – General Program Flow

Since this is a spreadsheet, the data and calculations are organized by type and function onto different “sheets” or tabs. Buttons on the sheets provide an alternate means of navigation between sections.

Where possible, the spreadsheet itself was used to perform the calculations. For example, the carbonate equilibria in the feedwater are handled in the spreadsheet. In addition, Langelier Saturation Index (LSI) and ASTM methods for CaSO_4 , SrSO_4 , BaSO_4 , and SiO_2 are also handled in the spreadsheet. However, the more detailed membrane performance and scaling calculations are

handled using a combination of iterative add-ins (Excel's Solver) and Visual Basic code specifically written for the purpose.

RO & NF Calculation Methods

General Approach

The general approach used is the same as used by most commercial membrane design programs. Basically the user needs to guess a design and then a detailed calculation is made. The TFSP program assists this process by continually displaying and updating an estimated feed pressure and TDS values for the user in the spreadsheet. This estimated pressure is the seed pressure for the start of the iterations. Final data display includes calculations for permeate, feed, net feed with recycle, and concentrate. Interested users can modify the program to display bank by bank data if they so desire.

The computational approach, although well understood conceptually, is more complicated in practice. The TFSP program makes one simplification over most commercial programs that greatly helps the calculation rates in that each vessel is converted to the form of one element, which directly returns the performance for each bank in the system. TFSP calculates salt flux on an ion-by-ion basis during each pass through the system and balances carbonates in the concentrate and permeate analyses while accounting for the free passage of CO₂ through the membranes. As an aside, the free passage of CO₂ is responsible for the significantly lower pH in the permeate as compared to the feedwater in most membrane systems.

Water flux, or more properly the flow rate, is calculated as follows, where Pi is osmotic pressure. The effective pressure or PNet is the net trans-membrane differential pressure. All values are first converted to meters, seconds, and atmospheres to make calculations simpler. Even though using a flow rate based on m³/sec results in small absolute numbers, the precision of the spreadsheet is more than sufficient to return accurate results. Data can be displayed in a variety of conventional metric or US units.

A review of some of the simpler membrane transport functions might be useful to understand the calculation process.

"A" value, or the water transport value, or simply the "water flux," is defined for each membrane type as water flow through the membrane per unit of membrane area per some pressure unit. For example:

Equation 1

$$"A" \text{ Value} = \frac{m^3/sec}{m^2 * atm} = \frac{m}{sec * atm}$$

Note that "A" value is dependent on pressure, which is of course the effective transmembrane pressure and the area, thus multiplying by the area and net pressure provides a direct calculation of the water flow rate through the membrane.

A Salt Flux coefficient, or "B" value is also generally defined as a salt passage rate or some unit of mass or volume per unit of membrane area. This reduces to a "velocity" type factor – i.e. m/sec. Note that the salt passage rate is almost entirely dependent on the concentration difference between both

sides of the membrane. Actually, “B” was originally defined as grams/(min*cm²). In any case, the mass or volume term later cancels so the actual unit of choice is irrelevant as long as consistency is maintained. B value combines terms for salt distribution and diffusion coefficients as well as membrane thickness as previously defined^{1,2}.

Equation 2

$$B \text{ Value} = \frac{m}{\text{sec}}$$

Both B and A are dependent on temperature and in some cases can be dependent on feed concentration, pH, and/or applied pressure. The corrections for pH are most important when considering the selectivity of TFC type membranes for silica transport or rejection. However, for most applications, a good approximation can be made if only temperature is considered.

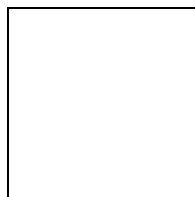
Combining the equations for A & B we get the familiar equation used to determine permeate concentration for each individual ion.

Equation 3



Similarly, using the familiar reverse osmosis transport equations, flow through the membrane at any point in the system can be expressed as follows:

Equation 4



Thus by combining the above equations for flow and permeate concentration, calculating a realistic concentration polarization, and calculating a transmembrane pressure which accounts for pressure losses through the system, we can compute the conditions for each individual element within the system.

The concentration of each ion in the permeate is found as follows. A variable, "MegDiff" is defined for each ion first which is the *effective* difference in concentration of the ion from the membrane surface to the permeate. This includes a factor for concentration polarization. Note also that the Bvalue is different for each ion. However, rather than define a separate value for each ion, it is customary to define a ratio to either sodium or chloride. Typically the ratio varies from 0.1 to 4, corresponding to a salt flux of 10% to 400% of the chloride rate.

Equation 5

$$MeqDiff = BulkLMAvg Conc * ConcPolarization - PermConc$$

Equation 6

$$PermConc_{ion} = MeqDiff_{ion} * \frac{BValue * BCorrectionByIon_{ion}}{PNet * AValue + BValue}$$

$$PermTDS = \sum_{all\ ions} PermConc(ion)$$

PNet is as defined above, i.e. the feed pressure less differential pressure less the osmotic pressure difference between the average feed stream and permeate. BcorrectionByIon is stored in the spreadsheet as a function of the membrane type selected. This is the ratio of salt flux for the ion in question relative to either chloride or sodium. This value is easily modified by the user to provide for special cases, or to even create new ions and coefficients.

Since the permeate concentration obviously affects the water flux and required pressure and vice versa, an iterative approach is necessary to solve the system. The general steps are as follows:

- a) Acquire a valid water analysis and target feed pH from the user supplied data. Read this data into the internal variables.
- b) Acquire flow and recovery information from the user via a graphic screen.
- c) Convert all flow rates to the internal flow scheme - TFSP uses m³/sec as the base flow units.
- d) Acquire from the user the suggested array, bank, and vessel layout and save in the internal variables. Typically, a system with higher recovery needs more banks. For example a 75% recovery system might specify 6 elements per vessel, 2 banks total in the array, and an array layout of 16:8. That is 16 vessels feeding 8 vessels in bank 2.
- e) Acquire from the user the selected membrane element information. When the user selects the type of element, the program loads the specific data about the element such as A value, B value, B values relative to Na or Cl per each ion (dependent on membrane type), area in m², differential pressure coefficients and so on. Membrane data is stored on the "Membrane Data" sheet. It is freely changeable and allows the user to create new elements as needed.
- f) Set up the selected membrane element in the vessel and calculate delta pressure and concentration polarization coefficients (called the "*BetaCoef*" in the code) for the selected elements. Delta pressure is calculated from a coefficient specific to the membrane configuration. The TFS program by default utilizes coefficients based on commercial membranes typical of those elements used for so called "pure water" applications. These assume water is the medium processed and assumes normal thickness feed size spacer materials. The user can adjust these coefficients for special elements as needed. Note that TFSP uses a simplified approach for this purpose. Given sufficient empirical data and physical dimensions, it is also quite feasible to calculate DP directly from using more rigorous techniques. However this requires physical data not usually obtainable from the manufacturers and the approximation below can be created from the tech data sheets provided by many manufacturers.

Equation 7

$$dp = dpCoef * \left(\frac{FeedFlow + ConcFlow}{2} \right)^{1.5}$$

Equation 8

$$ConcPolarization = CP = Exp(BetaCoef * Recovery)$$

The "BetaCoef" coefficient is unique to each physical configuration of the membrane and is generally determined empirically. The "recovery" value refers to the recovered water fraction in the unit or element of interest. The BetaCoef used by the TFSP was developed for single elements by using various commercial programs from the major manufacturers. By comparing the calculated concentration polarization values from these programs at a variety of conditions, an estimate of BetaCoef was made for four and eight inch diameter "generic" elements.

A physical means of visualizing the effect is to imagine that the spacer found in spiral membrane elements is more or less efficient at creating turbulence. If more efficient, then the mixing at the membrane's surface will be better and the concentration polarization will approach 1.0 more closely. With a BetaCoef = 0.0 there is no concentration polarization, i.e. CP = 1.0. Of course higher recovery in any given segment of the system or individual membrane element will lead to higher concentration polarization. The simple equation above has proven adequate for most design cases with "normal" flow parameters. A typical design maximum concentration polarization is normally in the range of 1.20 to 1.25 depending on the type of water being treated. For completely non-scaling waters, such as 2nd pass RO systems treating RO permeate, much higher concentration polarization values can be tolerated without inducing scale formation. This is of course a very simplified approach to computing the concentration polarization. Nevertheless it has proven useful in many commercial programs and it is more than adequate for prediction of concentrate concentrations to use for scaling calculations.

- g) At this point, calculations are ready to begin. The first step is to "Guess" the applied pressure needed to produce the water flow rate required. To do this the total membrane area in the system is calculated and the feed osmotic pressure is calculated. Based on nominal recovery and a nominal rejection for the element, a concentrate concentration is estimated by mass balance. The concentrate osmotic pressure is then calculated. Next a differential pressure is calculated for the first and last elements in the system and the average is used to calculate a differential pressure for the system. The "Guess" pressure needed is then calculated:

Equation 9

$$Guess(atm) = \frac{Flow}{A \text{ value} * Area} + Total_dp + \frac{FeedPi + ConcPi}{2}$$

N.B. - Flow is m³/sec, "A" value is m/(sec*atm) or m³/sec/m²/atm, dp and Pi in atm.

- h) Guess is the net pressure, which includes osmotic pressure and dp losses so the applied pressure is increased by average of the feed and concentrate osmotic pressures and the differential pressure. Osmotic pressure is calculated using the typical equation of state, summed for each ion in the analysis.¹ Total organic carbon contributions (if any) are ignored since the contribution is highly dependent on the type of organic carbon present.

Equation 10

$$OsmoticPressure(atm) = P_i = RT * \sum_{Allions} \alpha_i [c]_i$$

$$R = GasConst, T = \text{deg } K, \alpha_i = \text{activity coefficient}, [c]_i = \text{moles} / l$$

The Calculations for RO (reverse osmosis) and NF (nanofiltration) systems are arranged in a "Do While Loop" that starts with an assumed applied pressure. From this pressure, flow rates and concentrations are calculated on a vessel by vessel basis through the system. The total calculated flow is then compared to the target flow the user provided. If low, then the pressure is raised proportionally, and if high then the pressure is lowered proportionally. Once the calculated flow is within the set percentage of the target flow - typically 0.2% to 1% - then the calculation program terminates and data is returned to the spreadsheet for display.

- i) RO and NF calculations differ in approach to the transport of ions. For reverse osmosis systems, the permeate anions and cations are balanced equally. That is, any difference in overall charge in the first pass through the permeate concentration calculation (Equation 8) is split equally and the permeate concentration adjusted proportionally for each ion. For an NF system, the anions are assumed to control and the cations are adjusted to balance the permeate analysis.

Scaling Calculation Methods

ASTM Methods

Calculations for CaSO_4 , BaSO_4 , and SrSO_4 are taken from ASTM D 4692, Figures 1-3 respectively.² ASTM D4993 is the source for SiO_2 solubility.³ Langelier Saturation Index (LSI) is taken from the definition of LSI in the literature, which is consistent with data in Stumm and Morgan⁴ ASTM data was used for these common scale forming minerals since this the accepted industry method.⁵

Calcium Fluoride (CaF_2) is computed in a similar manner to the ASTM data except that the Ksp was taken from the Phreeqc database. The Van't Hoff method is used to correct for different temperatures.

Equation 11

$$\text{Van' tHoff Equation} = Ksp_{T_2} = Ksp_{T=25} - \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{298.16} \right)$$

$$R = GasConst, T_2 = \text{deg } K \text{ of solution}, K_{T=25} = Ksp \text{ at } 25^\circ C, \Delta H = \text{Enthalpy}$$

The ASTM methods are essentially polynomials derived by curve fitting techniques. These provide a Ksp value as a function of temperature and ionic strength (IS). The corrected Ksp is compared to the actual ion product for the stream of interest and a percent of solubility or percent of saturation is defined as follows. This method is also used for calcium fluoride.

$$\text{Percent Solubility} = \left(\frac{\text{Ion Product}}{Ksp \text{ corrected}} \right) * 100$$

Equation 12

The Langelier Saturation Index (LSI) is computed as follows:

$$LSI = pH - pH_s \text{ where}$$

Equation 13

$$pH_s = (pK_2 - pK_{So} + pCa + pAlk)$$

pH is the pH of the solution, "pH_s" is Langelier's calculated saturation pH. Thus a negative LSI indicates that CaCO₃ should not precipitate from solution.

- The values of pK₂ and pK_{So} are the carbonate solubility products and are corrected for temperature. pK₂ is corrected for ionic strength as well. Values were taken from Stumm & Morgan.⁴ -At 25 deg C, pK₂ ≈ 10.357, pK_{So} ≈ 8.48.
- pCa equals -log([Ca]) where [Ca] = calcium activity in moles/liter (activity can be thought of as an ionic strength-corrected concentration). Activities are computed using the Debye Huckel method.
- pALK equals -log([Total Alkalinity]), and Total Alkalinity = [HCO₃] + [CO₃] + [OH] – [H]. [HCO₃] and [CO₃] are also corrected for ionic strength.
- The value for carbonate (CO₃) is computed from [HCO₃] and pH.

It should be noted that LSI is not considered useful above an ionic strength of about 0.3. There are many excellent texts on LSI calculation so it will not be covered in further detail here.

Other Minerals

Less common minerals which are nevertheless of interest to membrane system designers are handled by the more rigorous aqueous complexation methods typical of the WaterEQ or Phreeqc programs (WATEQ4F, Plummer et al., 1976⁶, PHREEQE Parkhurst et al., 1980⁷, and Truesdell, 1974⁸). A given solution analysis is first numerically "speciated" into the various aqueous complexes that are present using thermodynamic stability constants. The saturation state of the solid is then calculated from the true solubility product, which is not a function of ionic strength, and the ionic concentrations determined from the speciation calculation.

After a careful consideration of many possible minerals, it was decided to limit the calculations and display to the minerals of most interest in the operating temperature and operating pH range of most membrane systems – i.e. 5 to 50 deg C, and pH 4 to 10.

The minerals of interest include:

- | | |
|--|--|
| • Analcime | NaAlSi ₃ O ₈ ·H ₂ O |
| • Gibbsite - aluminum hydroxide | Al(OH) ₃ |
| • Amorphous Al(OH) ₃ - aluminum hydroxide | Al(OH) ₃ |
| • Fe(OH) ₃ (amorphous) - Ferric hydroxide | Fe(OH) ₃ |
| • Goethite - Ferric hydroxide | FeO(OH) |
| • Siderite - Ferrous carbonate | FeCO ₃ |
| • Vivianite - Ferrous phosphate | Fe ₃ (PO ₄) ₂ ·8H ₂ O |
| • Hydroxyapatite - Calcium hydroxy phosphate | Ca ₅ (PO ₄) ₃ OH |
| • Gypsum (also by ASTM methods) - Calcium sulfate | CaSO ₄ ·2H ₂ O |
| • Sepiolite (High pH silica foulant) - Mag Silicate | Mg ₄ Si ₆ O ₁₅ (OH) ₂ ·6H ₂ O |

In a very simplistic sense, the approach is to create a list of all possible complex species which could exist in the solution, and then solve a set of equations describing these complexes based on known thermodynamic data for each complex

For example, for ferric iron, we consider the following aqueous species:

- $\text{Fe}^{3+} + \text{Cl}^- = \text{FeCl}^{++}$
- $\text{Fe}^{3+} + \text{SO}_4^- = \text{FeSO}_4^+$
- $\text{Fe}^{3+} + 2\text{OH}^- = \text{Fe}(\text{OH})_2^+$
- $\text{Fe}^{3+} + 3\text{OH}^- = \text{Fe}(\text{OH})_3(\text{aq})$
- $\text{Fe}^{3+} + \text{HCO}_3^- = \text{FeHCO}_3^+$
- $\text{Fe}^{3+} + \text{CO}_3^{--} = \text{FeCO}_3^+$
- $\text{Fe}^{3+} + \text{HPO}_4^{--} = \text{FeHPO}_4^+$
- $\text{Fe}^{3+} + \text{H}_2\text{PO}_4^- = \text{FeH}_2\text{PO}_4^{++}$

The solution to this set of equations provides the concentrations and activities of all species, including uncomplexed metal ion activities that are used to compute the ion products for the solids. These ion products are then compared to known Ksp values for the minerals of interest and a saturation index (SI) is calculated:

$$SI = \text{Log}\left(\frac{\text{Ion PRODUCT}}{Ksp}\right) = \text{Log}(IP) - \text{Log}(Ksp) \quad \text{Equation 14}$$

IP is also referred to as "Q", thus $SI = \text{Log}(Q) - \text{Log}(Ksp)$.

A negative SI value indicates under-saturation while a positive SI indicates over-saturation and possible precipitation. An SI of zero of course suggests the solution is exactly at saturation.

For example, Na and SO₄ form a complex with one negative charge - i.e. NaSO₄. The Log(Ksp) is calculated for this complex at the solution temperature on the sheet entitled LogKs. The formula for this complex is created as follows, where α represents the activity of the species under consideration. Activity values are calculated for each complex and each species on the sheet ActCof, and the "Available" concentration is determined on the sheet entitled "Calc".

$$[\text{NaSO}_4] = \frac{[\text{Na}]_{\text{available}} * \alpha_{\text{Na}} * [\text{SO}_4]_{\text{available}} * \alpha_{\text{SO}_4} * 10^{-\log Ksp}}{\alpha_{\text{NaSO}_4}} \quad \text{Equation 15}$$

Of course many other complexes containing both Na and SO₄ are also produced, and the amount available of each ion is affected by all of the other complexes. Because of this, the solution to the problem must be obtained iteratively. The Excel built in Solver is convenient for solving this problem. The program automatically implements a series of VBA commands which sets the Solver up and then runs it. The Solver continues to be invoked until the system of equations is solved to a degree of accuracy that is acceptable to the user.

For example, assume we wish to calculate the actual ion product for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the solution to determine the scaling potential. We calculate the actual and available concentrations as follows.

| Species | Ca(molal) | SO ₄ (molal) |
|-----------------------------------|-----------|-------------------------|
| Actual Conc | 0.00374 | 0.01041 |
| Available Conc | 0.00292 | 0.00885 |
| Activity coefficient (α) | 0.447 | 0.447 |

We then calculate the $\text{Log}(K_{sp})$ for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in this solution and temperature to be -4.59. The logarithm of the ion product for CaSO_4 based on the concentration available is compared to the $\text{Log}(K_{sp})$ to provide an SI.

$$SI = \text{Log}(0.00292 * 0.447 * 0.00885 * 0.447) - \log(K_{sp})$$

Equation 16

$$SI = -5.29 - (-4.59) = -0.70$$

Thus at this condition, CaSO_4 is significantly undersaturated. Since the SI is log based, the percent of saturation is $10^{(-0.7)} = 0.1995$ or about 20%. In this example, the ASTM method, which uses a K_{sp} corrected for ionic strength with typical analyses yielded a value of about 21% of saturation. Thus the ASTM method compares very well and slightly conservatively in this case. As an aside, this points out the big difference in comparing solubility using percent of saturation values as compared to SI's. SI's are logs so some confusion is possible when comparing different systems.

Nevertheless, it should be noted that the calculations performed using the ion complex method are performed for minerals that may actually supersaturate to a very high degree, and thus not cause problems in many membrane system applications. The aluminum and iron compounds investigated are almost always present to some degree in surface and ground waters. This program provides the user a means to effectively determine the optimum pH conditions to minimize potential fouling from these compounds. However, the user should note that iron and aluminum compounds are usually present in the amorphous condition and the fouling or non-fouling tendencies of the compounds may be greatly dependent on the presence or absence of organic or biological components in the feedwaters. The organic and biological components may act either to solublize or precipitate them, depending on the water conditions and nature of the organics present.

Carbonate Equilibrium

The calculation of the appropriate carbonate and pH distribution is an important part of this program. Note that membrane systems readily pass carbon dioxide (CO_2) while carbonate (CO_3^{2-}) is strongly rejected. Thus the permeate side of the membrane is enriched with carbon dioxide while the feed/concentrate side of the membrane is enriched with carbonate and bicarbonate. The net effect of this separation is to lower the pH of the permeate while the concentrate pH rises. The TFSP program effectively models this behavior. For applications in which a membrane system precedes a deionization (DI) system, the additional carbon dioxide can pose a load on the anion resins. The TFSP program can help the user to evaluate the use of acid versus scale inhibitor or softening resins as the pretreatment step.

The steps necessary to calculate the carbonate equilibrium are as follows:

- a) The solution ionic strength is calculated, defined as

$$IS = 0.5 * \sum_{\text{All Ions}} [\text{Ion}] * \text{Abs}(z)$$

Equation 17

- b) pK1 and pK2 are corrected for the solution temperature.

Ionic strength corrections are then applied to pK1 and pK2. The methods are described in Stumm and Morgan.⁴

- c) pK1 and pK2 are converted back to K1 and K2 values.

- d) The [H⁺] concentration is calculated from solution pH

The Mole Fraction (fraction of the total inorganic carbon) for HCO₃ is calculated from K1, K2, and pH. If the HCO₃ concentration was specified then the Total Inorganic Carbon (TIC) is calculated from the mole fraction of HCO₃. If TIC was specified then the concentration of HCO₃ is calculated using the mole fraction of HCO₃.

$$\text{MoleFraction } HCO_3 = \left(\frac{(H^+)}{K1} + 1 + \frac{K2}{H^+} \right)^{-1}$$

Equation 18

$$\text{Total Inorganic Carbon} = TIC = \frac{[HCO_3]}{\text{MoleFraction } HCO_3}$$

- e) Knowing the Total Inorganic Carbon (TIC), we then calculate the CO₂ and CO₃ values from pH and K1 and K2 as follows. The values are in moles/liter.

$$[CO_3] = TIC * \left(\frac{(H^+)^2}{K1 * K2} + 1 + \frac{H^+}{K2} \right)^{-1}$$

Equation 19

$$[CO_2] = TIC * \left(\frac{(K1)^2}{H^+} + 1 + \frac{K1 * K2}{(H^+)^2} \right)^{-1}$$

- f) For the treated feed - i.e. the feed with the pH adjusted, we have already computed the Total Inorganic Carbon (TIC) and thus the new carbonate distribution can be readily calculated from the equations above. The amount of acid required is easily computed from the change in bicarbonate concentration from the user-supplied feed water to the treated feed water composition.

Scale Inhibition and Scale

Computing the likelihood of scale formation using the TFSP is a straightforward matter. Today, the membrane designer has a wide variety of scale prevention techniques and products available that potentially allow a system to operate at supersaturated conditions. The original scale inhibitor of choice in membrane systems was sodium hexametaphosphate or SHMP. This has the advantage of being relatively nontoxic, cheap, easily soluble in water, and reasonably effective with carbonates and sulfates. Unfortunately, it also begins to hydrolyze immediately upon dissolution so the active life of the material is poor and this has led to many inadvertent failures in RO systems over the years. Phosphonate or polymer-based scale inhibitors with superior performance and no degradation in solution have come to replace SHMP in most applications.

Traditionally, membrane systems operated at lower pH's to avoid damage to the cellulosic membranes and to avoid calcium carbonate precipitation. This usually necessitated acid addition, a moderately dangerous practice. Today, many systems completely avoid the need for pH control even in the presence of moderate calcium carbonate concentrations through the use of phosphonate or polymer based scale inhibitors. In fact, operating LSI's of 2 or even higher are routinely obtained with readily available scale inhibitors at moderate doses – typically 2-3 ppm in the feed.

In addition, operation of systems that have a proclivity toward calcium, barium, and strontium sulfate scaling have become routine as well. With many of the newer phosphonate type scale inhibitors, for example those based on aminotris(methylenephosphonic acid) (AMP), concentrate levels of calcium sulfate corresponding to an SI of 0.4 or higher (250% of normal solubility) can be safely obtained if certain operational parameters are observed. Poly acrylic acid (PAA) polymers give slightly less protection.

Three mechanisms of action for typical membrane industry scale inhibitors are usually recognized.

- Threshold
- Dispersion
- Crystal Distortion

Threshold inhibitors are typically represented by the phosphonates, such as AMP and related compounds. Threshold inhibitors are believed to function by absorption onto specific areas of a crystal that is just beginning to grow, retarding or preventing its growth. Thus the crystal can never grow large nor connect with other crystals that are in solution or are already precipitated on the membrane. Typical doses are in the order of 15 - 25 ppm in the concentrate at maximum effectiveness.

Crystal distortion mechanisms are similar to threshold inhibitors except that they work by distorting the crystal during growth. Photomicrographs of crystal distorters at work are particularly striking, showing round or irregular crystals. The prototypical crystal distorter is a long-used scale inhibitor known as polyacrylic acid (PAA) polymer.

Dispersants are useful with both crystal distorters and threshold agents. These are typified by carboxylic acid polymers such as polymaleic acid (PMA) or phosphonobutane tricarboxylic acid (PBTC).⁹ Since threshold agents may produce very small, microscopic crystals, if any at all, a dispersant is warranted for optimum fouling control.

Affect of Iron and Aluminum

Iron and aluminum compounds are considered in the TFSP calculations. Normally very insoluble relative to compounds such as calcium sulfate, they are usually only present in low concentrations anyway. However, the presence of iron can decrease the effectiveness of a threshold or distorter agent by reacting or complexing with the agent, thus hindering its ability to prevent scale. Scale inhibitor doses for threshold agents in particular must be increased in the presence of iron. With high iron concentrations, increased inhibitor dose combined with a dispersant type agent can effectively prevent scale formation even in under severe conditions.

The presence of iron or aluminum compounds above their solubility limits thus is not limiting but suggests that additional scale inhibitor may be required. Many commercial programs already

account for this affect, which can be substantial.¹⁰ TFSP can assist the membrane designer in assessing the possibility of iron or aluminum fouling in a given feedwater.

Summary and Conclusions

The Total Flux and Scaling Program (TFSP), written for Excel 97 and above, provides designers operators, and educators new tools to predict membrane system performance, including scaling and fouling parameters, for a wide variety of membrane system configurations and feedwaters. Of special significance, the program provides scaling calculations for mineral species not normally addressed in commercial programs, including aluminum, iron, and phosphate species. In addition, ASTM calculations for common predicted species such as calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), BaSO_4 , SrSO_4 , SiO_2 , and LSI are also provided. The spreadsheet is fully transparent, allowing the operator to manually change all aspects of the program.

The TFSP development was funded under EPA contract 9C-R193-NTSX and is freely downloadable at www.reverseosmosis.com/download/TFSP.zip, or by contacting Thomas Speth at Speth.Thomas@epa.gov. Mention of trade names or commercial products in this article and spreadsheet does not constitute endorsement or recommendation for use by the U.S. Government.

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